Appendix L. Chemical Analytical Method
MITC – sorbent tubes
California Department of Food and Agriculture Laboratory

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MITC in Air Samples By GC/NPD

Scope: This method was developed to analyze MITC from air sample tubes using GC/NPD. The reporting limit is 0.2 µg per sample.

Principle: MITC (Methyl Isothiocyanate), CH_3-N=C=S, that has been absorbed from the air onto activated charcoal is desorbed from the charcoal with 0.1% CS_2 in ethyl acetate and analyzed by gas chromatography using a Nitrogen Phosphorus Detector (NPD).

Reagents and equipment:

Reagents:

1. Carbon disulfide, nanograde
2. MITC (CAS registry # 556-61-6)
   Standard 1 mg/mL in 0.1% CS_2 in ethyl acetate: obtained from Standards Repository, CDFA, Center for Analytical Chemistry, 3292 Meadowview Road, Sacramento, California 95832
3. Charcoal tubes: Lot # 120, SKC #226-09
   SKC, 334 Valley View Road, Eighty Four, Pennsylvania 15330
   To request tubes: (800) 752-9378
4. Ethyl acetate, Fisher, pesticide grade

Equipment:

1. Test tubes, 25 mL, with Teflon lined caps
2. Assorted pipettes and micro syringes
3. Volumetric flasks
4. Small triangular file
5. Thermolyne Vortex Maxi Mixer II
6. Forceps
7. Plug puller, Supelco # 2-0596
8. Nylon Acrodiscs®, 0.2 µm, Gelman Sciences
9. HP 6890 with NPD
10. HP 6890 with 5973 Mass Selective Detector

Analysis:

Sample Extraction:

1. Remove samples from freezer and allow them to warm to room temperature.
2. Fold a white sheet of paper into quarters, reopen and place it under the tube to catch any spilled charcoal.
3. Break both ends of each charcoal tube with a file and a plug puller.
4. Score each charcoal tube with a file in front of the glass wool plug, and then break the tube.
5. Use a 9" disposable pipette to push all tube material into a test tube containing 5 mL of 0.1% CS_2 in ethyl acetate and cap the tube immediately.
6. Allow samples to desorb for 30 minutes and vortex them occasionally.
7. Filter the mixture through a Nylon Acrodisc and collect it in an autosampler vial.
8. Analyze samples on GC with NPD.
9. Spike: Follow steps 3 and 4 to break the tube. Spike a known amount of MITC through glass wool onto the center of charcoal. Follow steps 5-8 to do extraction.
10. Confirmation will be performed on GC/MSD with SIM (ions 73, 45, 58), if required.

Instrument Conditions:

HP 6890 equipped with dual NPD

Column:	FFAP, 10 m x 0.53 mm x 1.0 μm
Gas flow rate:	Constant flow (Helium) at 9.0 mL/minute
	Hydrogen: 3.0 mL /minute
	Air flow: 60.0 mL/minute
	Carrier + make-up: 12.0 mL/minute
Injector:	220°C
Detector:	250°C
Oven temperature:	Initial temp.: 45°C for 7 minutes
	Rate: 40°C/minute
	Final temp.: 200°C for 1 minute
Injection volume:	2 μL
Retention time:	~5.8 minutes

HP 6890 equipped with 5973 mass selective detector

Column:	HP-5MS, 30 m x 0.25 mm x 0.25 μm
Gas flow rate:	Constant flow (Helium) at 1.0 mL/minute
Injector:	200°C
Oven temperature:	Initial temp.: 50°C for 8 minutes
	Rate: 30°C/minute
	Final temp.: 250°C for 2 minutes
Injection volume:	1 μL
Retention time:	~3.2 minutes

Analysis: continued

Calculations:

Quantitate the amount of MITC present in a charcoal tube as follows:

µg/sample =(sample peak height) (final volume of sample)/(response factor)
where:

FV	= 5 mL
Response Factor	= [Σ (std peak ht_n/std $conc._n$)]/n
n	= number of standards

Method Performance:

Quality Control:

1. A six point standard curve of 0.025, 0.05, 0.1, 0.5,1.00 and 5.00 µg/mL, was obtained at the beginning and the end of each set of samples for calculating the response factor and checking instrument performance.
2. A sample set is usually comprised of 10 samples, a blank and a spike. Standards and samples were injected twice sequentially to insure reliability for the analysis.

Recovery Data:

Validation: Method validation was done by spiking charcoal tubes with three different levels of standard (0.4, 3 and 8 µg) on five separate days. A matrix blank was also run each day. The recovery data is summarized in the table below:

Recoveries of MITC

Spike level (µg)	set 1 (%)	set 2 (%)	set 3 (%)	set 4 (%)	set 5 (%)
0.4	83.8	91.2	89.0	104.3	86.4
3	82.4	88.4	96.0	102.8	87.9
8	84.7	85.7	77.0	80.8	80.6

Method Detection Limit (MDL):

Method detection limit refers to the lowest concentration of analyte that a method can detect reliably in either a sample or blank. To determine the MDL, seven charcoal tubes were spiked separately with 0.15 µg of MITC by following procedure #9 in the sample extraction section. These spiked samples along with a blank were then analyzed using the described method. The standard deviation derived from the seven spiked samples was used to calculate the MDL using the following equation:

$$\mathbf{MDL = t\,S}$$

Where:

t: is the Student 't' value for the 99% confidence level with n-1 degree of freedom (In this case **t** is 3.143).

S: is the standard deviation obtained from the recovery (µg) of replicate analyses.

Method Detection Limit (MDL): continued

Sample MDL's

Sample No.	µg Spiked	µg Recovered
1	0.15	0.1314
2	0.15	0.1292
3	0.15	0.1245
4	0.15	0.1297
5	0.15	0.1191
6	0.15	0.1295
7	0.15	0.1211

Average µg recovered = 0.1264
Standard Deviation = 0.0048
The calculated MDL for MITC is 0.02 µg/sample.

Method Performance:

Reporting Limit:

Reporting limit refers to the level above which quantitative results may be obtained. In this method, the reporting limit was set at 0.2 µg/sample.

Discussion:

MITC is unstable, reactive and sensitive to oxygen. Adding solvent to the charcoal is exothermic and may cause loss of MITC. Cap the tube well during extraction.

An analytical run consists of a solvent blank, a matrix blank, duplicate injections of samples and a six point standard curve. The calculation of recovery is based on the height of peak.

The reporting limit is 0.2 µg/sample. This is revised from the 1998 revision of 0.4 µg/sample. New instrumentation with better sensitivity allows this improvement.

Reference:

ICI Americas Inc., "Methyl Isothiocyanate from Metham-Sodium Determination in Air" # RRC-82-35, August 26, 1982.

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